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STUDY OF THE THERMAL PROPERTIES AND SOME REACTIONS OF SILVER FLUORIDES

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ABSTRACT

The thermal properties of silver fluoride and silver subfluoride were studied by derivative thermal analysis and by X-ray analysis. From the results, conclusions were drawn on the decomposition mechanism.

The thermal behaviour of silver fluoride–alkali halide systems was studied. It was established that silver fluorides react with the alkali halides.

INTRODUCTION

In studying the thermal behaviour of silver fluorides, various authors have obtained apparently contradictory results.

According to our present knowledge, the melting point of silver fluoride (AgF) is 433[1] or 435 °C[2] and the boiling point is 1147 °C[3]. Gunz and Wöhler[4] on heating an aqueous solution of silver fluoride have obtained a greenish substance, which on the basis of analysis was found to be silver subfluoride.

Wöhler and Rodenwald[5] found that if silver subfluoride (Ag_2F) is heated in nitrogen or carbon dioxide atmosphere, a gray opaque mass is formed between 90 and 115 °C, which consists of silver fluoride and metallic silver.

Several authors made similar observations, finding that Ag_2F decomposes at 100 °C[6], 90 °C[7] and between 100 and 200 °C[8,9]. Hettich[10] observed the formation of elemental fluorine on stronger heating. Bródy and coworkers[11] could not verify the liberation of fluorine on dry heating at 600 and 800 K and at a fluorine vapour pressure of 0.1 and 10 Torr. In the presence of moisture hydrogen fluoride and oxygen are probably formed[9].

In view of the ambiguous data in the literature, we decided to study the thermal behaviour of silver fluorides. Within the scope of this work we studied also the thermal behaviour of silver fluoride and alkali halide mixtures.

EXPERIMENTAL

Silver fluoride used was a Carl Roth OHG (Karlsruhe) product; silver subfluoride was prepared by electrolysis in our laboratory. According to X-ray analysis (Fig. 2), both fluorides contained small amounts of silver and silver oxide as impurity. Alkali halides used in studying the above reactions were Reanal (Budapest) products.

The derivatograms were recorded on a Paulik–Paulik–Erdey Model MOM derivatograph in the presence of air. The gasous products formed were removed by an ejector from the reaction zone. About 800 mg of material was weighed into a platinum crucible (upper diameter 9 mm). The heating rate was 4.7 °C min^{-1}.

The X-ray diffractograms were taken on a Müller-Micro 111 X-ray diffractometer and recorded on a Phillips Model PW-1051 recorder under conditions as follows: radiation Cu/Ni, excitation: 40 KW 18 mA, voltage of GM tube: 1625 V, speed of detection 0.5 °C min^{-1}, slit system: 1°–0.2–1°, attenuation: 16, time constant: 4 sec, speed of chart: 400 mm h^{-1}.

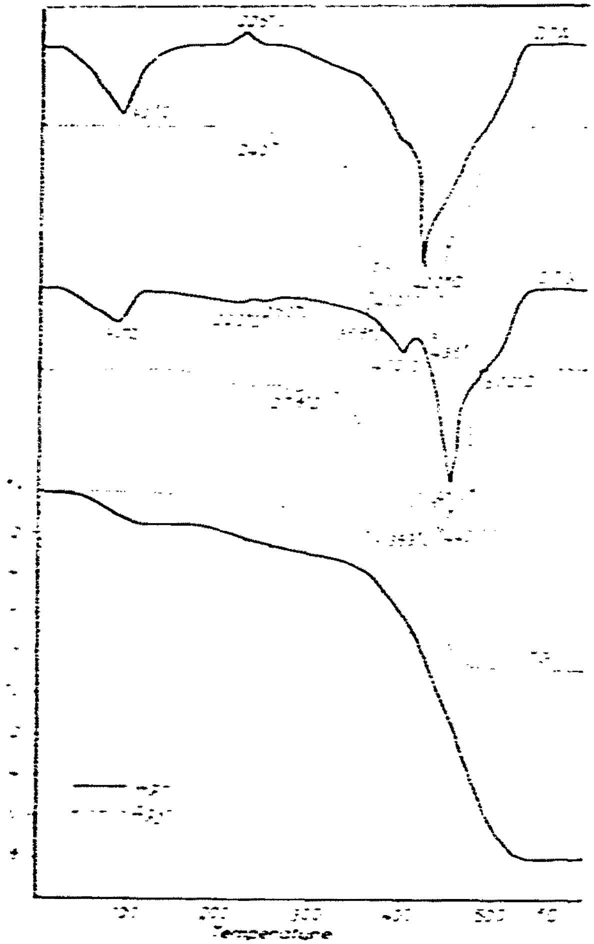


Fig. 1. Derivatogram of silver fluorides.

RESULTS AND DISCUSSION

(*A*) *Thermal properties of silver fluorides*

In Fig. 1 the derivatograms of silver fluoride and silver subfluoride are compared. According to the derivatograms, the decomposition of these compounds proceeds in several steps. To clear the decomposition mechanism, the heating of silver fluorides was interrupted at different breaking points of the DTG and DTA curves and the X-ray diffractograms of the decomposition residues and of the starting materials were taken (Fig. 2).

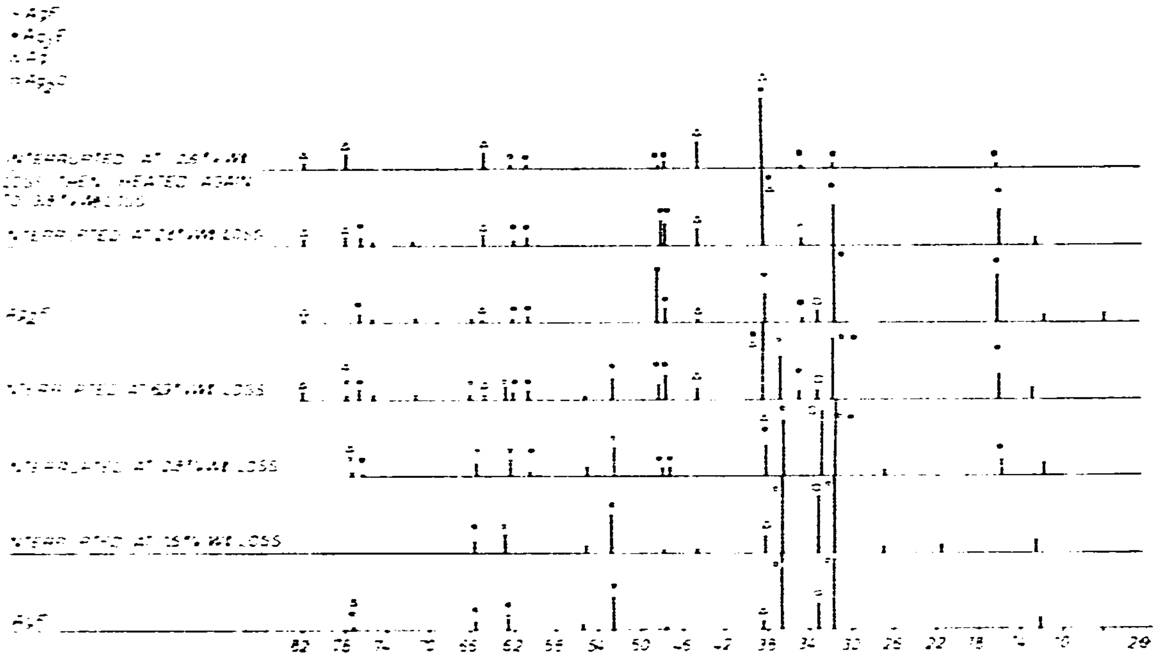


Fig. 2. X-ray diffractograms of the decomposition residues of samples heated to different temperatures.

(*1*) *Silver fluoride*

The X-ray diffractogram of silver fluoride, heated up to 120°C (weight loss: 1.5%) does not exhibit substantial changes, as compared to the non-heated substance (Fig. 2). This means that no compounds with new structure were formed during the process characterized by the DTG peak at 90°C (Fig. 1).

The weight loss and enthalpy change observed in this step are due to the loss of adsorbed water, which was proved by the determination of the water content of the sample.

The X-ray diffractogram of the substance heated up to 270°C (weight loss: 2.8%) showed in addition to the increase of the intensity of lines characteristic of silver and silver oxide new bands characteristic of silver subfluoride. The intensity of the lines of silver fluoride decreased on the X-ray diffractogram. The diffractogram indicates the beginning of two dissociation processes. In one of them, silver and fluorine are formed, in the other silver subfluoride and fluorine.

The exothermic peak on the derivatogram at 225 °C indicates the oxidation at maximum speed of the metallic silver formed during dissociation.

The X-ray diffractogram of the substance heated up to 410 °C (weight loss: 6.9%) exhibits an increase in the intensity of the lines of silver difluoride. A decrease in the intensity of the silver oxide line and a further increase in the intensity of lines characteristic of metallic silver can also be observed. The increase in the amount of metallic silver comes partly from the thermal decomposition of silver oxide and partly from that of fluorides. The DTG peak at 400 °C on the derivatogram (Fig. 1) is indicative of the maximum speed of the conversion into silver difluoride. This conversion, however, does not proceed quantitatively.

The DTA peak at 420 °C indicates the melting of silver fluoride not yet converted[1,2]. When melting proceeds at maximum speed, the sample has lost already about 40% of its fluorine content. Above 400 °C, already silver subfluoride dissociates. The involved processes overlap.

The thermal reactions can be described as follows:

(a) The adsorbed water is removed in the first step:

$$AgF\cdot xH_2O \xrightarrow{90^\circ} AgF + xH_2O$$

(b) The decomposition of silver fluoride begins which proceeds only partially in the temperature range between 90 and 520 °C.

$$2AgF \xrightarrow{90-520\ ^\circ C} 2Ag + F_2$$

(c) A part of the silver fluoride is converted at 400 °C with maximum speed to silver subfluoride.

$$2AgF \xrightarrow{400\ ^\circ C} Ag_2F + \tfrac{1}{2}F_2$$

(d) Silver subfluoride, formed in the above reaction, decomposes on further heating. Decomposition takes place with maximum speed at 450 °C.

$$Ag_2F \xrightarrow{450\ ^\circ C} 2Ag + \tfrac{1}{2}F_2$$

Side reactions occur too in the decomposition of silver fluoride.

(e) Silver, formed below 200 °C, oxidizes into silver oxide at 225 °C.

$$4Ag + O_2 \xrightarrow{225\ ^\circ C} 2Ag_2O$$

(f) The silver oxide formed decomposes at 240 °C.

$$2Ag_2O \xrightarrow{240\ ^\circ C} 4Ag + O_2$$

(2) *Silver subfluoride*

Its derivatogram (Fig. 1) is similar to that of silver fluoride. Essential difference can be observed on the DTA curves. Thus, the DTA peak at 358 °C can be seen only on the DTA curve of silver subfluoride. A slight loss in weight can also be observed parallel to the change in enthalpy, but it does not result in a new DTG peak. To study the process in detail, heating of the sample was interrupted at 370 °C. The X-ray diffractogram of the cooled product (Fig. 2) shows that the intensities of the silver subfluoride lines have decreased, while that of metallic silver has increased, indicative of the fact that the dissociation of silver subfluoride into silver and fluorine has begun parallel to the process proceeding without loss in weight. Repeated heating the sample up to 370 °C, the DTA peak at 358 °C appears again and again, as long as the sample contains fluorine, showing that the conversion studied is reversible.

As the course of the derivatogram above 360 °C is similar to that of silver fluoride, it is assumed that the reversible reaction taking place at 358 °C is the dissociation reaction of silver subfluoride into silver fluoride and metallic silver. The stability of silver fluoride formed by the thermal process is lower, therefore its decomposition at maximum speed takes place at a lower temperature (383 °C) and with higher yield (in the step of 383 °C nearly half of the fluorine content is lost), than that of the stable silver fluoride (400 °C) chosen as a starting material.

The thermal reactions taking place in the thermal decomposition of silver difluoride are as follows:

(a) Below 340 °C a very small part of silver subfluoride dissociates into silver and fluorine

$$Ag_2F \xrightarrow{270-340\,^{\circ}C} 2Ag+F$$

(b) At 358 °C another dissociation process occurs at maximum speed

$$2Ag_2F \xrightarrow{358\,^{\circ}C} 2AgF+2Ag$$

(c) At 383 °C silver fluoride formed in the above reaction is converted again into silver subfluoride releasing fluorine

$$2AgF \xrightarrow{383\,^{\circ}C} Ag_2F+\tfrac{1}{2}F_2$$

(d) At 440 °C silver subfluoride dissociates into silver and fluorine

$$Ag_2F \xrightarrow{440\,^{\circ}C} 2Ag+\tfrac{1}{2}F_2$$

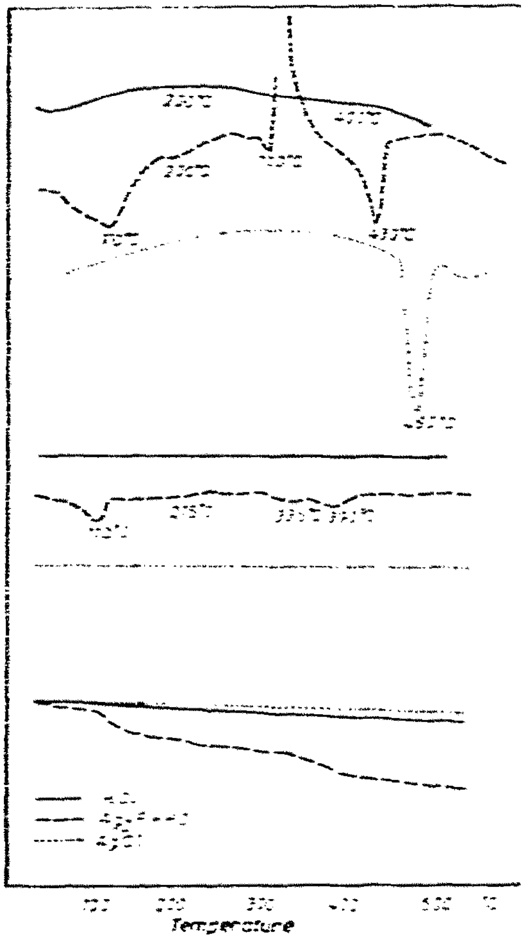
Thus, we did not detect near 100 °C silver subfluoride on heating solid silver fluoride as Gunz and Wöhler[4] have, on heating aqueous solution of the substance. Under our experimental conditions, silver subfluoride was formed only above 120 °C. The maximum speed of this process was reached at 400 °C.

The formation of silver fluoride, on heating silver subfluoride in the presence of air, was detected by means of the DTA curve at 358 °C, but due to the reversibility of the process we were not able to detect silver fluoride in the cooled sample, as contrary to the observations of Wöhler and coworkers[5], who have obtained at 90–115 °C silver fluoride from silver subfluoride in nitrogen or carbon dioxide atmosphere.

All this shows that the thermal behaviour of silver fluoride is greatly affected by the experimental conditions and that experiments carried out under different conditions result in apparently contradictory results. The problem is made more difficult by the alternating transformation of silver fluorides into each other, and by the overlap of the consecutive processes.

(B) *Reaction of silver fluorides with alkali halides*

Figures 3, 4 and 5 show the derivatograms of the 1:1 molar mixtures of silver subfluoride and alkali halides, compared to those of the components and of the corresponding silver halide, recorded under the same conditions.



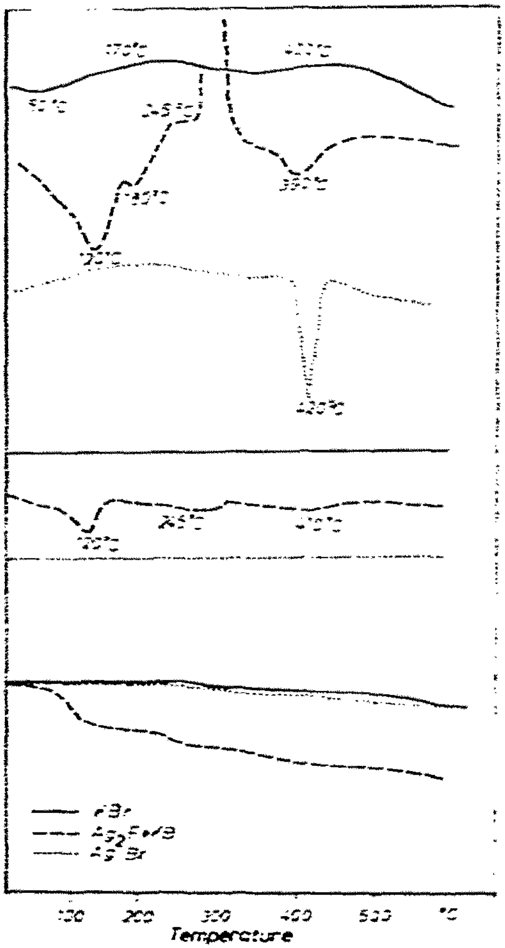


Fig. 3 (left). Study of the reaction of Ag_2F–KCl.

Fig. 4 (right). Study of the reaction of Ag_2F–KBr.

In Fig. 3 the DTA curve of the mixture of Ag_2F–KCl exhibits a sharp exothermic maximum, and simultaneously the endothermic peak at 358 °C, due to the dissociation of Ag_2F, disappears. The maximum is a result of interaction. The endo-

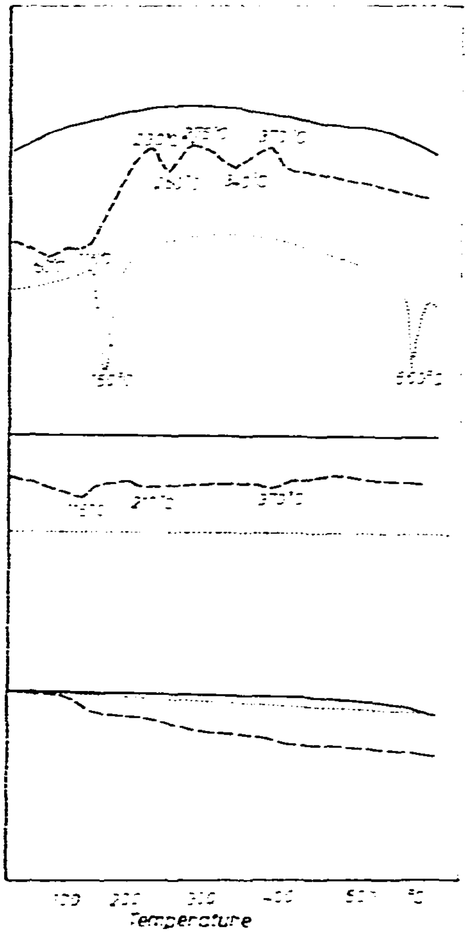


Fig. 5. Study of the reaction of Ag_2F–KI. (—) KI, (---) Ag_2F+KI and (···) AgI.

thermic process at 430 °C, indicating a melting point (with melting-point depression) permits to conclude on the formation of silver chloride (see the derivatogram of silver chloride).

In the case of the Ag_2F–KBr mixture (Fig. 4), the exothermic peak, indicating the interaction, appears at a lower temperature (300 °C). The endothermic process observed at 390 °C, is associated with the melting of the silver bromide, formed during the reaction (see the derivatogram of AgBr).

While Ag_2F reacts with potassium chloride and bromide in a violent exothermic reaction, the interaction with potassium iodide occurs at a lower temperature and in a milder form. Moreover, the process occurs in several steps. Remarkably, the DTA curve does not indicate formation of silver iodide: the peak characteristic of the melting of silver iodide was not observed at 560 °C.

On studying the 1/1 molar mixture of silver fluoride and alkali halide, new exothermic peaks appeared on the diagrams, showing the reaction between the components. The reactions take place between 200 and 300 °C, *i.e.* at a slightly lower temperature than in the case of silver subfluoride. (It is remarkable that the oxidation of silver fluoride was observed in the same temperature range). Ag_2F reacted with potassium iodide, while AgF with potassium chloride in the mildest form (the reactions are indicated by a relatively small exothermic peak).

The derivatograms permit only in the case of certain alkali halides the conclusion, that silver halide and potassium fluoride are formed in the oxidation–reduction process between silver subfluoride and alkali halides and in the simple exchange reaction between silver fluoride and alkali halides.

For a more detailed study of the reaction mechanism, heating of mixtures of silver fluoride and alkali halide was interrupted after the exothermic reaction, and the X-ray diffractograms of the residues were taken (Fig. 6). Silver bromide and silver iodide were identified on the diffractograms of the residues of the mixtures containing potassium bromide and potassium iodide, but we could not identify silver chloride in the residue of the mixture containing potassium chloride. The reaction was indicated only by the appearance of the potassium fluoride line and some foreign lines. We did not find the lines characteristic of potassium fluoride in the product of the reaction between silver fluoride and potassium iodide. It is worthy to note that we could not identify silver iodide in the residue on heating the mixture of silver subfluoride and potassium iodide (Fig. 5), silver chloride on heating the mixture of silver fluoride and potassium chloride, and potassium fluoride on heating the mixture of silver fluoride and potassium iodide (Fig. 6). On the basis of these observations and the new lines not yet identified (Fig. 6) shown on the diffractograms, it may be assumed that not only silver halide, potassium fluoride and silver metal are formed in the reactions between silver fluorides and alkali halides but other complexes (presumably K[AgX] or Ag[AgX]) too, which may represent intermediates in the formation of silver

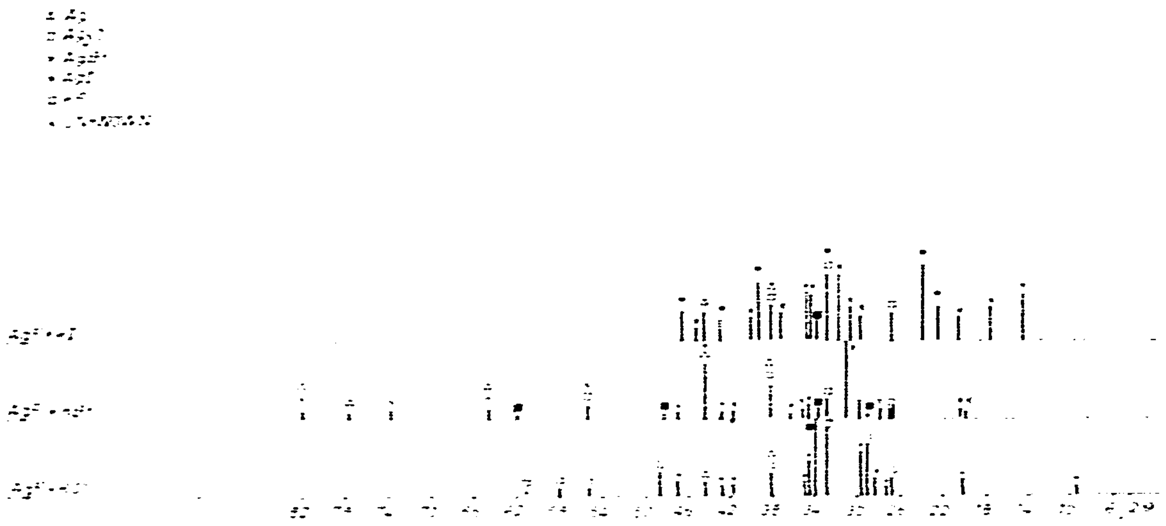


Fig. 6. X-ray diffractograms of the heat-treated mixtures of AgF and alkali halides.

halides. The thermal stability of these intermediates may determine whether at the temperature studied silver halide is present in the system, or not.

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